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Commentary on the sphalerite geobarometer

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ABSTRACT

The FeS content of sphalerite in assemblages with pyrite and pyrrhotite has been widely used and widely criticized as a geobarometer. The commonly accepted form of the geobarometer is based on the composition of sphalerite being independent of temperature below about 550 °C at all pressures up to at least 10 kbar, but strong thermodynamic arguments require a significant temperature dependence in this region. Most minor components have a negligible effect on the relevant equilibria, but the effect of CuS is somewhat more significant. Molar and partial molar volumes for binary (ZnS-FeS) and ternary (ZnS-FeS-CuS) sphalerite solutions are presented; the ternary data are consistent with charge transfer between Cu and Fe. Difficulties in the application of the sphalerite geobarometer also arise from failure to consider adequately the paragenetic implications of textural relations among the minerals involved. An example from Ducktown, Tennessee, demonstrates the importance of nonequilibrium features and their interpretive value. Based on commonly occurring minerals of simple chemistry, sound theory, favorable kinetic factors, and a considerable body of experimental data, the sphalerite geobarometer requires only careful application and resolution of the remaining conflict between theory and experiment to provide an extraordinarily useful tool in the interpretation of geologic processes over time.

INTRODUCTION

For almost two decades, the term "sphalerite geobarometer" has been used for the interpretation of the Fe content of sphalerite in assemblages containing pyrite + pyrrhotite as a measure of physical pressure of equilibration (Scott, 1973, 1976; Brown et al., 1978; Hutcheon, 1978; Lusk et al., 1975; Ethier et al., 1976; Scott et al., 1977; Moles, 1983; Shimizu and Shimazaki, 1981; Oberhänsli et al., 1985; and many others). Serious questions have arisen with regard to its theoretical basis (see, e.g., Banno, 1988; Kalogeropoulos, 1983, raises similar questions about related interpretations of the composition of sphalerite) and variable results (see, e.g., Stumpfl, 1979, 1980).

In this paper we shall consider first the Fe-Zn-S phase diagram in terms of temperature and pressure, then the effects of other components (especially Cu) on the phase diagram, and finally, some geologic considerations concerning the application of the phase diagram to rocks. Although the similar equilibrium in the assemblage sphalerite + troilite + Fe (the sphalerite cosmobarometer) has been applied to meteorites (Schwarcz et al., 1975; Hutchison and Scott, 1983; Kissin et al., 1986), we shall not discuss this specifically.

STATUS OF THE Fe-Zn-S PHASE DIAGRAM

Experimental studies

The first extensive experiments on sphalerite phase equilibria at low pressure were those of Kullerud (1953), who also made computations of the effect of increased pressure. Kullerud's results were significantly modified by Barton and Toulmin (1966), but the phase diagram was still limited to the vapor-present region, and the portion below about 580 °C was based on extrapolation of data obtained at higher temperatures. Boorman (1967), Chernyshev and Anfilogov (1967, 1968), Chernyshev et al. (1968), and Scott and Barnes (1971) made direct experimental studies of the low-pressure equilibrium pyrrhotite + pyrite + sphalerite down to about 300 °C, and Scott and Kissin (1973) extended qualitative understanding of the system to even lower temperatures. The realization that temperature was secondary to pressure in controlling the composition of sphalerite in assemblages with pyrite and pyrrhotite incited further experimental investigation of the role of pressure (Scott, 1973, 1976; Lusk and Ford, 1978; Hutchison and Scott, 1981), and thus the sphalerite geobarometer was put on a footing that encouraged widespread geological application.

Low-temperature natural experiments

Even at low pressure, the data for the Fe-Zn-S phase diagram below about 300 °C are conflicting in several respects. Skinner et al. (1967) noted sphalerite containing

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16.6 mol% FeS formed at 325 ± 25 °C with pyrite and pyrrhotite in samples from the Salton Sea geothermal area. Similarly, in their study of sphalerite in the Broadlands, New Zealand, geothermal field, Browne and Lovering (1973) clearly demonstrated that relatively Fe-poor sphalerite (7.1 ± 0.6 and 9.8 ± 0.9 mol% FeS at 219 and 253 °C, respectively) had precipitated with pyrite and pyrrhotite at pressures of less than 100 bars. Groves et al. (1975) found sphalerites with average FeS content of 10.6 mol% associated with pyrite and pyrrhotite in nickel ores recrystallized at low temperature. Scott and Kissin (1973) produced a schematic low-temperature phase diagram based on both experimental study and natural samples, which also implied the existence of low-Fe sphalerite in equilibrium with pyrite and pyrrhotite.

In contrast, Barton et al. (1977) found sphalerite with up to 20 mol% FeS in a pyrite-bearing but pyrrhotite-free deposit at Creede, Colorado, which had abundant evidence from fluid inclusions for deposition at low pressure and at temperatures in the range of 190 to 290 °C. The significance of these observations is strengthened by those of P. M. Bethke (personal communication, 1972) and D. M. Pinckney and G. A. Desborough (personal communication, 1972), who found up to 20 mol% FeS in sphalerite from the Upper Mississippi Valley lead/zinc district. The presence of pyrite without pyrrhotite implies a lower value of a_{FeS}, and hence a lower FeS content in the associated sphalerite than does a pyrrhotite-bearing assemblage, so even higher FeS contents would be required for sphalerite in the geobarometer assemblage of pyrite + pyrrhotite + sphalerite. It is possible (indeed, likely) that the pyrite in these examples was not deposited at the same time as the sphalerite (pyrrhotite certainly was not present). If so, then the observations are not in conflict with the phase diagram developed by Scott, Kissin, Browne, and Lovering. One is then left, however, without an explanation of why earlier pyrite would not have been altered to pyrrhotite during a later high-FeS stage of mineralization. A most promising line of research would be to seek out and analyze additional sphalerite from carefully documented mineral assemblages in modern geothermal systems or unmetamorphosed ore deposits having reliable, independent thermometry.

Thermodynamic considerations

As mentioned previously, experimental studies of the equilibrium assemblage sphalerite + pyrite + pyrrhotite at temperatures below about 550 °C have shown essentially constant, i.e., temperature-independent, composition of sphalerite. From a thermodynamic point of view this is puzzling, as it requires several independent quantities to vary systematically in such a way as to cancel their separate effects. It is true that, at low pressure, the pyrite + pyrrhotite equilibrium below 550 °C occurs at nearly constant values of a_{FeS} (Toulmin and Barton, 1964, Fig. 8). This coincidence is specific for a particular pressure, however. The equations governing the effect of pressure on a_{FeS} along the pyrite + pyrrhotite equilibrium require, for any reasonable set of properties of the participating phases, that the pressure effect on the FeS content of sphalerite will be greater at low temperature than at high temperature. Calculations of the effect of pressure on the sphalerite + pyrite + pyrrhotite equilibrium have been carried out by Scott (1973, 1976), Hutcheon (1978, 1980), Gamble (1978), Stowell (1989), and others, all of whom have used essentially the equations derived by Barton and Toulmin (1966). All of these calculated phase diagrams exhibit an increasingly strong temperature effect on the Fe content of sphalerite in equilibrium with pyrite and pyrrhotite as pressure increases, in conflict with the experimental evidence previously cited. In an attempt to resolve this problem, we have reevaluated the calculations.

Reconsideration of the problem of the effects of pressure on the composition of sphalerite has revealed an error (nonfatal) in the treatment by Barton and Toulmin (1966). The first equality in their Equation 2 is inexact: the constancy (over the compositional range of interest) of $\bar{V}^{\mathrm{sp}}_{\mathrm{FeS}}$, the partial molar volume of FeS in sphalerite, does imply that the partial derivative of the logarithm of the activity coefficient with respect to pressure at constant temperature, $(\partial \ln \gamma^{\mathrm{sp}}_{\mathrm{FeS}}/\partial P)_T$, is independent of composition, but this constancy does not require that the partial derivative equal the isothermal total derivative with respect to pressure $(\mathrm{d} \ln \gamma^{\mathrm{sp}}_{\mathrm{FeS}}/\mathrm{d}P)_T$, as they stated. Because of this, the simplified versions of their Equation 1 used to evaluate pressure effects on the univariant equilibria involving troilite + Fe + sphalerite and pyrite + pyrrhotite + sphalerite are invalid, and the full evaluation of their Equation 1 must be carried out, taking into account the variation of $\ln \gamma^{\mathrm{sp}}_{\mathrm{FeS}}$ with composition and with pressure. We do this by substituting the total derivative

$$(\mathrm{d} \ln \gamma^{\mathrm{sp}}_{\mathrm{FeS}}/\mathrm{d}P)_T = (\partial \ln \gamma^{\mathrm{sp}}_{\mathrm{FeS}}/\partial P)_{\mathrm{T},N\mathrm{FeSsp}} + (\partial \ln \gamma^{\mathrm{sp}}_{\mathrm{FeS}}/\partial N^{\mathrm{sp}}_{\mathrm{FeS}})_{T,P}(\mathrm{d}N^{\mathrm{sp}}_{\mathrm{FeS}}/\mathrm{d}P)_T \quad (1)$$

into Equation 1 of Barton and Toulmin (1966),

$$(\mathrm{d}N^{\mathrm{sp}}_{\mathrm{FeS}}/\mathrm{d}P)_T = (1/\gamma^{\mathrm{sp}}_{\mathrm{FeS}})[(\mathrm{d}a_{\mathrm{FeS}}/\mathrm{d}P)_T - a_{\mathrm{FeS}}\,(\mathrm{d} \ln \gamma^{\mathrm{sp}}_{\mathrm{FeS}}/\mathrm{d}P)_T] \quad (2)$$

which leads to

$$(\mathrm{d}N^{\mathrm{sp}}_{\mathrm{FeS}}/\mathrm{d}P)_T = \frac{(1/\gamma^{\mathrm{sp}}_{\mathrm{FeS}})(\mathrm{d}a_{\mathrm{FeS}}/\mathrm{d}P)_T - N^{\mathrm{sp}}_{\mathrm{FeS}}(V^{\mathrm{sp}}_{\mathrm{FeS}} - V^{0}_{\mathrm{FeS}})/\mathrm{R}T}{1 + N^{\mathrm{sp}}_{\mathrm{FeS}}(\partial \ln \gamma^{\mathrm{sp}}_{\mathrm{FeS}}/\partial N^{\mathrm{sp}}_{\mathrm{FeS}})_{T,P}}. \quad (3)$$

Experimental data are available (Barton and Toulmin, 1966; Toulmin and Barton, 1964) to evaluate this expression. Taking into account the corrected values for $(\mathrm{d}a_{\mathrm{FeS}}/\mathrm{d}P)_T$ (Scott, 1973, p. 471), the numerical results are (perhaps unsurprisingly) essentially unchanged from those reported earlier: "$\mathrm{d}N^{\mathrm{sp}}_{\mathrm{FeS}}/\mathrm{d}P$ at constant temperature [is] approximately −1 mole percent FeS per kilobar . . . at 742 °C, increasing [*sic*] to approximately −3 mole percent FeS per kilobar at 325 °C" (Barton and Toulmin, 1966, p. 847).

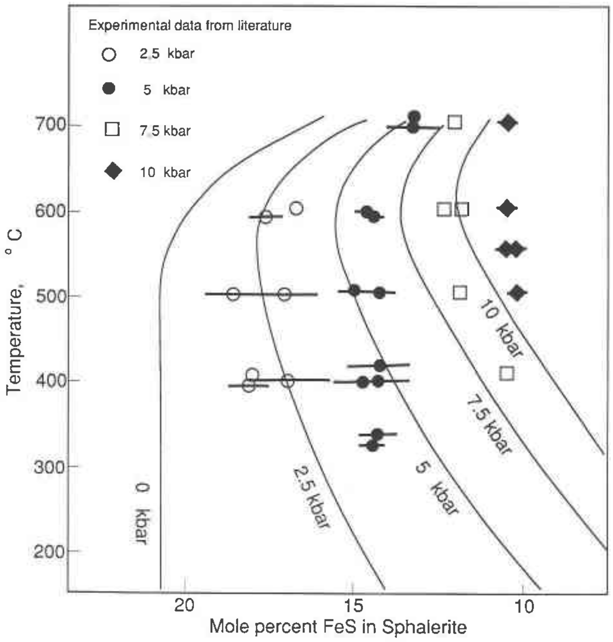


Fig. 1. Portion of the phase diagram for the system Fe-Zn-S, showing the composition of sphalerite in equilibrium with pyrite and pyrrhotite, as a function of temperature at pressures up to 10 kbar. Zero-kbar isobar from Scott (1973); isobars for higher pressures calculated as described in the text, independent of experimental data. Experimental points from Scott (1973, 1976) and Lusk and Ford (1978).

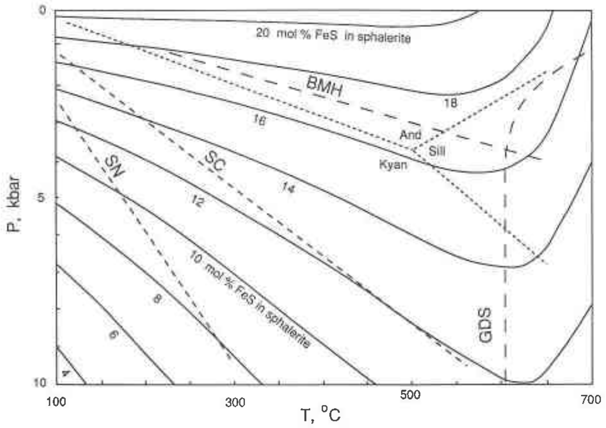


Fig. 2. *P-T* projection of sphalerite compositions, with some petrologic and geologic reference curves. Thin solid lines are contours of N^{sp}_{FeS}; thin broken lines are field boundaries between the Al_2SiO_5 polymorphs andalusite (And), kyanite (Kyan), and sillimanite (Sill) (Holdaway, 1971); thin dashed line (GDS) is the H_2O-saturated granodiorite solidus; heavy broken lines are geothermal gradients (BMH = Battle Mountain High, Nevada; SC = typical stable craton; SN = Sierra Nevada) (Lachenbruch and Sass, 1978, Fig. 9-5).

We have carried out a numerical integration of this relation in order to examine the shape of the solvus curve at high pressures. In our procedure we have taken into account the compressibility and thermal expansion of all phases involved, and have used two different initial (zero-pressure) conditions: (1) the vertical ($dn/dT = 0$ below about 520 °C) solvus discussed previously and (2) an alternative calculated from the pyrite-pyrrhotite solvus and the thermodynamic properties of sphalerite solid solutions. The results are qualitatively the same: with increasing pressure, the effect of temperature on the FeS content of sphalerite becomes more pronounced (or, alternatively, at temperatures below about 500 °C, the effect of pressure is increased markedly by lower temperatures). The results (initial Condition 1) are shown in Figure 1, along with the experimental determinations cited. The results of this recalculation retain the strong curvature of the isobaric solvus lines, in accord with earlier calculated diagrams but in conflict with experimental data. We wish to emphasize that all studies of the thermodynamic properties of this system lead to predictions of a significant isobaric temperature effect on the composition of sphalerite in equilibrium with pyrite and pyrrhotite at temperatures below 450–500 °C at high pressure. Only by establishing the reality of this dependence, or the reasons for the lack of it, will the sphalerite geobarometer be put on a satisfactorily firm basis. The reason for the discrepancy between calculation and calibration below 400 °C is unknown to us, but experimentation with refractory phases like sphalerite or pyrite at low temperatures is notoriously difficult, and thermodynamic extrapolation of results from higher temperature may be a more trustworthy guide to the truth. On the other hand, the calculations assume that the phases interacting at low temperatures (and high pressures) are the same as those on which the extrapolations are based and that their properties vary smoothly. If new phases with substantially different properties intervene, the calculations would represent metastable equilibria that might depart significantly from those governing the natural assemblages.

Figure 2 shows the calculated phase relations in a *P-T* projection, which helps set the sphalerite geobarometer in a geological context. It is easy to envision geologically reasonable *P-T-t* (pressure-temperature-time) trajectories that cross sphalerite composition contours in either or both directions, or that are nearly parallel to them. The possibilities for complex sequences of compositional changes are qualitatively obvious, and with the acquisition of better quantitative data on reaction rates and mechanisms, numerical modeling of such variations offers exciting potential (Mizuta, 1988a, 1988b).

The data required to calculate the sphalerite geobarometer (by which, again, we mean the compositions of pyrrhotite and sphalerite, both stably coexisting with pyrite and with each other, as a function of temperature and pressure) were derived as follows. For the activity coefficient of FeS in sphalerite, we used the expression for a_{FeS} derived by Craig and Scott (1974, Fig. CS16; corrected for an obvious drafting error: "−" should be "×") from the data of Barton and Toulmin (1966), Scott and Barnes (1971), and Scott and Kissin (1973). The pyrrhotite solvus, or composition of pyrrhotite in equilibrium with pyrite (in the system FeS-S_2), at zero pressure, was taken from a least-squares fit to the smoothed data of Toulmin and Barton (1964, Table 5), which yielded

$$\ln N^{po}_{FeS} = -1.5182 \times 10^{-4}T + 1.7404 \times 10^{-7}T^2 - 1.2538 \times 10^{-10}T^3.$$

This function reproduces the data in Table 5 of Toulmin and Barton (1964) with an rms deviation of 0.0002 in N^{po}_{FeS}. The molar volume of pyrrhotite was obtained as a linear function of composition by least-squares refinement of volumes calculated from cell-edge determinations by Toulmin (unpublished data), Haraldsen (1941), Taylor (1970), and Fleet (1968). The resulting expression for the molar volume (2 g atoms) of pyrrhotite, V^{po} (cm^3) $= 26.412 - 8.1925N^{po}_{FeS} \pm 0.009$ (1σ) ($n = 34$; $r^2 = 0.95$), corrects the expression given by Toulmin and Barton (1964, Table 7), which is seriously in error as to the effect of the S_2 component. For this study, the (composition-independent) partial molar volumes of FeS (18.219 cm^3) and S_2 (26.412 cm^3) in pyrrhotite were corrected for temperature and pressure by applying coefficients of thermal expansion of 1.22×10^{-4} K^{-1} (298–593.15 K) and 6.75×10^{-5} (593.15 K and above) and of compressibility (-0.002 $kbar^{-1}$) (Skinner, 1966; Birch, 1966). Higher-order functions calculated from the equations of Novikov et al. (1982) do not lead to significantly different results within their range of applicability (below 200 °C; they cannot be successfully extrapolated to high temperatures and pressures).

The molar volume of pyrite was obtained from the room-conditions value 15.962 cm^3 mol^{-1} [2 g atoms, or ⅔(FeS_2)] (Robie et al., 1978; Toulmin and Barton, 1964) and the values for thermal expansion and compressibility given respectively by Skinner (1966) and Birch (1966). Molar and partial molar volumes of sphalerite and its components were derived as described later in this paper, and corrected for temperature and pressure by the equation of Skinner (1962) and the compressibility given by Birch (1966), both for pure ZnS.

Bryndzia et al. (1988, 1990) and Bryndzia and Scott (1986) have proposed a geobarometer based on their extensive experimental study of the compositions of coexisting sphalerite and hexagonal pyrrhotite at pressures from 1 to 6 kbar. Their experimental data define pyrrhotite and sphalerite compositions well within the pyrite-absent field at the relevant temperatures and pressures, consistent with the calculated equilibria and experimental data on the pyrite-pyrrhotite-sphalerite reaction discussed in this paper.

ROLE OF OTHER COMPONENTS

The sphalerite structure is well known for its ability to accommodate a variety of substitutions, leading to solid solution of many components, among them CdS, MnS, HgS, CoS, NiS, ZnSe, ZnO, $CuFeS_2$, and Cu_2FeSnS_4, in addition to FeS. It is commonly assumed, on the basis of rather sketchy experimental evidence, that most divalent cations (Cd^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, etc.) substitute ideally; i.e., the volumes are additive, and the various components do not affect one another's partial molar volumes. For the most part, the molar volumes of the components are sufficiently similar that the distinction between additive volumes ($V \propto N$) and additive cell edges ($V \propto \sqrt[3]{N}$) is well within experimental error, and either model is in agreement with the data available in most such systems. We therefore conclude that the presence of geologically normal concentrations of such components as CdS, MnS, ZnSe, CoS, and the like does not affect the partial molar volume of FeS in sphalerite, or the geobarometer based on that component. In the case of CdS, furthermore, Scott (1973) cites experiments by A. J. Hartlein showing that the sphalerite phase relations are not changed by the presence of several weight percent of this component. CuS, however, behaves in a somewhat more complex manner, as we shall see below.

The effect of the CuS component on the sphalerite geobarometer could operate in two ways: by affecting the partial molar volume of FeS in either pyrrhotite or sphalerite, or by changing the activity coefficients for Fe- or Cu-bearing components in the sphalerite solid solution. The latter factor is probably unimportant because the phase equilibrium studies of Toulmin (1960), Wiggins and Craig (1980), Hutchison and Scott (1981), and Kojima and Sugaki (1984) indicate that at low pressures and at temperatures of 600 °C and below, the FeS content of sphalerite in equilibrium with pyrite and pyrrhotite is not significantly changed by CuS activity corresponding to saturation with iss (intermediate solid solution, the high-temperature phase at the composition of chalcopyrite). The effect of CuS on the partial molar volume of FeS in pyrrhotite cannot be evaluated quantitatively on the basis of present data, but we expect it to be small, in view of the relatively small shifts in d_{102} and the high values of N_{FeS} in Cu-bearing pyrrhotites (see Yund and Kullerud, 1966, Fig. 4). Furthermore, d_{102} values for a series of synthetic pyrrhotites equilibrated with pyrite and the iss phase at temperatures from about 300 °C to 550 °C are indistinguishable from those of Cu-free pyrrhotites of the same FeS content, though at 550 °C and above (the data extend to about 650 °C) the two data sets diverge (Barton, unpublished data).

With respect to sphalerite, however, CuS has a more significant effect on the partial molar volume of FeS, and we have a moderate body of data with which to evaluate it. Toulmin (1960), in a preliminary report on a study of the phase relations of Cu-Fe-bearing sphalerites equilibrated with pyrite, pointed out that the substitution of Cu in Fe-bearing sphalerites reduces the length of the unit-cell edge. Wiggins and Craig (1980), in a more elaborate reconnaissance of phase relations in the system Cu-Fe-Zn-S, confirmed this observation and presented an empirical equation describing the variation of a with composition of sphalerite in the system ZnS-FeS-CuS. We have combined the data of these two studies to derive an expression for the molar volume of Cu-Fe-bearing sphalerites.

TABLE 1. Values of unit-cell edges for Cu-Fe-bearing sphalerite

Mol%			cm × 10^{-8}		
FeS	ZnS	CuS	a_{obs}	a_{calc}	Δa
58.98	36.43	4.59	5.4123	5.4109	0.0014
33.23	59.63	7.14	5.4121	5.4119	0.0002
2.55	96.09	1.36	5.4129	5.4104	0.0025
34.85	61.30	3.85	5.4117	5.4155	−0.0038
6.32	90.11	3.57	5.4120	5.4119	0.0001
6.62	92.22	1.16	5.4104	5.4122	−0.0018
4.98	94.51	0.51	5.4118	5.4117	0.0001
4.93	93.61	1.46	5.4115	5.4114	0.0001
7.50	92.00	0.50	5.4129	5.4130	−0.0001
7.41	91.05	1.54	5.4124	5.4124	0.0000
9.92	89.06	1.02	5.4138	5.4137	0.0001
9.87	88.62	1.51	5.4136	5.4133	0.0003
12.47	86.96	0.57	5.4153	5.4151	0.0002
12.41	86.53	1.06	5.4147	5.4146	0.0001
12.35	86.11	1.54	5.4145	5.4142	0.0003
14.92	84.55	0.53	5.4163	5.4162	0.0001
14.84	84.13	1.03	5.4157	5.4156	0.0001
14.94	83.56	1.50	5.4150	5.4152	−0.0002
19.94	79.56	0.50	5.4181	5.4181	0.0000
19.74	78.76	1.50	5.4171	5.4167	0.0004
19.45	77.62	2.93	5.4160	5.4151	0.0009
24.53	74.49	0.98	5.4188	5.4189	−0.0001
24.02	72.95	3.03	5.4160	5.4158	0.0002

Note: Data are in addition to the data of Barton and Toulmin (1966); all were used in the derivation of Equation 6. Compositions are in mole percent, unit-cell lengths in Å. Calculated cell edges are values corresponding to molar volumes calculated from Equation 6, using 6.0220943 × 10^{23} mol^{-1} for Avogadro's number. The value Δa is the difference $a_{obs} - a_{calc}$. Values above the horizontal line were determined by Wiggins; those below the line, by Toulmin.

Molar and partial molar volumes of sphalerite components

The cell-edge data for Fe-bearing sphalerites used by Barton and Toulmin (1966) to derive an equation for the variation of a with composition (equation shown in their Fig. 2) can be fit equally well by a symmetrical regular-solution model for molar volume (Thompson, 1967):

$$V_m = V^0_{\mathrm{ZnS}} N_{\mathrm{ZnS}} + V^0_{\mathrm{FeS}} N_{\mathrm{FeS}} + W_V N_{\mathrm{ZnS}} N_{\mathrm{FeS}} \tag{4}$$

the resulting parameters are [for (Zn,Fe)S] $V^0_{\mathrm{ZnS}} = 23.828 \pm 0.008\ \mathrm{cm}^3$, $V^0_{\mathrm{FeS}} = 24.022 \pm 0.028\ \mathrm{cm}^3$, $W_V = 0.5654 \pm 0.024\ \mathrm{cm}^3$.

The situation is more complex with regard to Cu substitution in sphalerite because of uncertainties as to valence ($\mathrm{Cu}^{2+} + \mathrm{Fe}^{2+}$ vs. $\mathrm{Cu}^{+} + \mathrm{Fe}^{3+}$) and its effect on metal-S bond lengths. The extent of Cu substitution in sphalerite is enhanced by the presence of other ions, especially Fe and Sn, in such a way as to suggest at least partially coupled substitution (Toulmin, 1960; Wiggins and Craig, 1980). We have no reason to suspect that Cu-bearing sphalerite departs significantly from the high degree of stoichiometry with respect to metal-S proportions that was established for the Fe-Zn-S system by Barton and Toulmin (1966, p. 834 and Fig. 9).

The measurements by Toulmin in Table 1 were made on synthetic charges prepared at 666 °C, consisting solely of sphalerite and pyrite. Starting materials were synthetic ZnS-FeS solid solutions, synthetic CuS, and synthetic pyrite. Total bulk composition of the charges was known, and the composition of the sphalerite calculated on the assumption that the pyrite contained neither Cu nor Zn. Absence of phases other than sphalerite and pyrite was determined by both optical and X-ray diffraction examination. In a few cases, the compositions so determined were later checked by microprobe analysis and found to be in agreement. Unit-cell edges were determined by X-ray diffraction with Ni-filtered Cu*K* radiation, using high-angle peaks (one to four of the following *hkl*: 533, 620, 531, 440, 511, and 422) and an internal standard (CaF_2, a = 5.4634 Å).

For the purposes of this paper, these data were combined with the large data set (for sphalerite synthesized at S activities greater than that provided by the buffer Fe + troilite) used by Barton and Toulmin (1966, Fig. 2) for the FeS-ZnS join. Least-squares regression of unit-cell volume against composition led to a satisfactory fit for a polynomial of the form

$$V = A + BN_{\mathrm{FeS}} + CN_{\mathrm{FeS}^2} + DN_{\mathrm{CuS}} + EN_{\mathrm{CuS}^2} + FN_{\mathrm{CuS}} N_{\mathrm{FeS}}. \tag{5}$$

This was algebraically transformed to the formulation for a symmetrical regular solution (Thompson, 1967):

$$V = V^0_{\mathrm{ZnS}} N_{\mathrm{ZnS}} + V^0_{\mathrm{FeS}} N_{\mathrm{FeS}} + V^0_{\mathrm{CuS}} N_{\mathrm{CuS}} + W_{\mathrm{ZnS}} N_{\mathrm{FeS}} N_{\mathrm{CuS}} + W_{\mathrm{FeS}} N_{\mathrm{ZnS}} N_{\mathrm{CuS}} + W_{\mathrm{CuS}} N_{\mathrm{ZnS}} N_{\mathrm{FeS}}. \tag{6}$$

The coefficients for this expression are as follows:

$$V^0_{\mathrm{ZnS}} = 23.830\ \mathrm{cm}^3 \pm 0.001\ (1\sigma)$$

$$V^0_{\mathrm{FeS}} = 24.034\ \mathrm{cm}^3 \pm 0.016$$

$$V^0_{\mathrm{CuS}} = 41.446\ \mathrm{cm}^3 \pm 2.106$$

$$W_{\mathrm{ZnS}} = -26.735\ \mathrm{cm}^3 \pm 2.123$$

$$W_{\mathrm{FeS}} = -17.977\ \mathrm{cm}^3 \pm 2.102$$

$$W_{\mathrm{CuS}} = 0.54253\ \mathrm{cm}^3 \pm 0.014.$$

It should be emphasized that we do not assign any particular physical significance to these quantities other than their role in Equation 6. Although Equation 6 accurately describes the variation of volume in sphalerite solid solutions, the extrapolated values of these properties to unrealizable end-member compositions do not correspond to any real phase.

The quantities of greatest interest in the present context are the partial molar volumes, $\bar{V}$, of FeS and CuS in sphalerite, for these determine the variation with pressure of the partial molar Gibbs free energies, or chemical potentials, of these components (or of any other components, e.g., CuFeS_2, that may involve these components). In terms of the mole fractions of FeS and CuS, the partial molar volumes are given by

$$\bar{V}_{\mathrm{FeS}} = V^0_{\mathrm{FeS}} + W_{\mathrm{FeS}} (N_{\mathrm{CuS}})^2 + W_{\mathrm{CuS}} (1 - N_{\mathrm{FeS}})^2 + (\Delta W) N_{\mathrm{CuS}} (1 - N_{\mathrm{FeS}}) \tag{7}$$

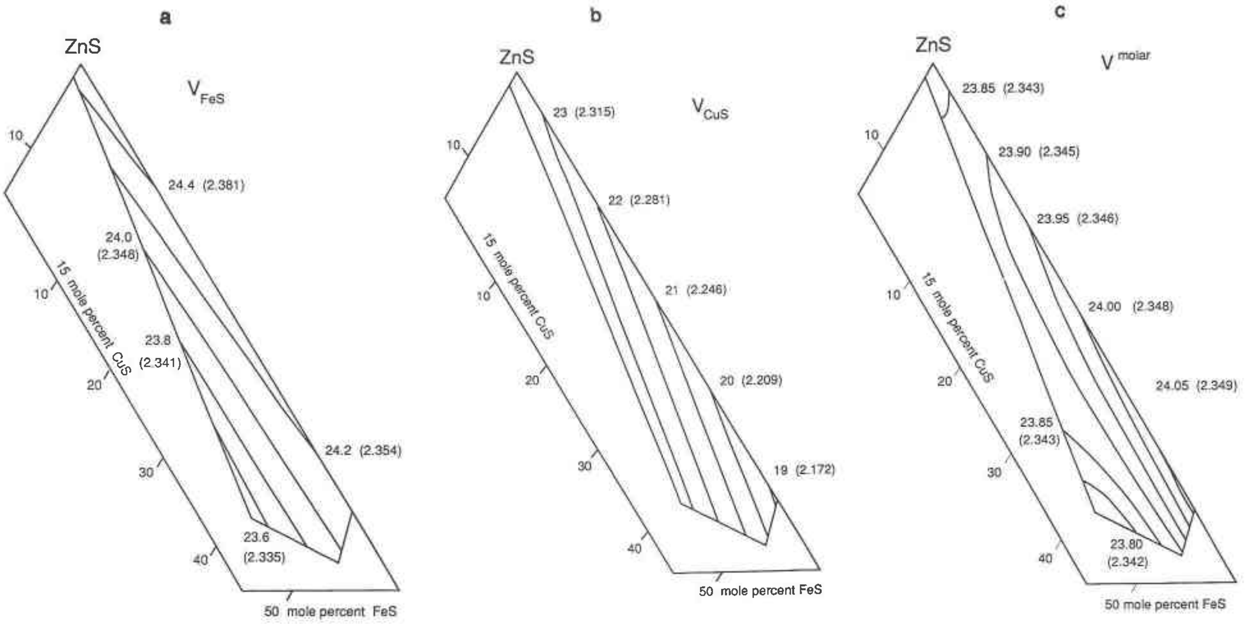


Fig. 3. Sphalerite molar and partial molar volumes. Contours are labeled in units of cm³ per formula unit of 2 g atoms and (in parentheses) the corresponding values of metal-S interatomic distances, in Å. **(a)** V^{sp}_{FeS} (Fe-S); **(b)** V^{sp}_{CuS} (Cu-S); **(c)** V^{molar} [(Zn,Fe, Cu)-S].

and

$$\bar{V}_{CuS} = V^0_{CuS} + W_{CuS}(N_{FeS})^2 + W_{FeS}(1 - N_{CuS})^2 + (\Delta W)N_{FeS}(1 - N_{CuS}) \qquad (8)$$

where $\Delta W = (W_{ZnS} - W_{FeS} - W_{CuS})$. The partial molar volumes are contoured in Figure 3; it should be noted that the contour intervals in the two parts of the figure are very different, and the variation in $\bar{V}_{CuS}$ is much greater than that in $\bar{V}_{FeS}$.

Although the uncertainties in some of the parameters of the molar volume equation are relatively large, these uncertainties are highly correlated (Clifford, 1973); the uncertainties in derived quantities (i.e., partial molar volumes in this instance) are significantly smaller than might be thought. A detailed evaluation by the methods of Clifford (1973, especially p. 67 and 79) shows that the expected errors (1σ) in $\bar{V}_{FeS}$ and $\bar{V}_{CuS}$ vary in a complex way with composition but are less than 2% throughout the field of stability of sphalerite: the average is about 1.2% for $\bar{V}_{FeS}$ and 1.3% for $\bar{V}_{CuS}$.

Effect on the sphalerite geobarometer

The value of $\bar{V}_{FeS}$ essentially controls the pressure sensitivity of the FeS content in sphalerite; it should be noted that the variation, though small, is such that addition of CuS to the sphalerite should enhance the solubility of FeS in sphalerites at high pressures. Hence a given FeS content in a Cu-bearing sphalerite implies a higher pressure than it would in a Cu-free assemblage.

Accurate evaluation of the effect of pressure on sphalerite compositions in the quaternary system Cu-Fe-Zn-S requires more detailed thermodynamic data for the participating phases than are available. Qualitatively, the decrease in $\bar{V}^{sp}_{FeS}$ with Cu content should enhance the Fe content of sphalerite at higher pressures. If we assume that $\bar{V}^{po}_{FeS}$ is essentially unchanged by the addition of Cu to pyrrhotite up to the saturation point with intermediate solid solution (iss), we may take the value of $(\bar{V}^{sp}_{FeS} - V^0_{FeS})$ in Equation 3 to be approximately 5.5 cm³ mol⁻¹ FeS for a sphalerite in equilibrium with pyrite, pyrrhotite, and iss, rather than the 6 cm³ mol⁻¹ used in the Fe-Zn-S system. This change does not significantly alter the results. In view of the relatively slight shift in FeS content of sphalerite between the Cu-free and iss-saturated systems (Toulmin, 1960; Wiggins and Craig, 1980), it seems very likely that Cu has only a very slight effect on the predicted sphalerite compositions at low temperatures and high pressures in environments saturated with pyrite + pyrrhotite + (± chalcopyrite). The reciprocal-temperature term in the pressure coefficient still predominates, the FeS content of sphalerite must still decrease, and the interpretation of experimental results (Scott, 1973; Lusk and Ford, 1978) as requiring a temperature-independent value of N^{sp}_{FeS} remains in conflict with this result.

Crystal-chemical interpretation

In addition to their thermodynamic significance, partial molar volumes shed some light on the crystal chemistry of the phases and atomic species involved. The values of the partial molar volumes of the FeS and CuS components represent the incremental megascopic volume effects of varying sphalerite composition toward the respective components, the effective volume of a mole of the pure FeS or CuS component in sphalerite of the given

TABLE 2. Mean tetrahedral bond distances in some copper-iron sulfide structures

	Fe-S	Cu-S
Chalcopyrite (Hall and Stewart, 1973)	2.257 Å	2.302 Å
Cubanite (Szymanski, 1974a)	2.280	2.305
Cubanite (2 shorter bonds)	2.261	
Covellite (Evans and Konnert, 1976)	—	2.312
High cubanite, disordered Fe_2Cu (Szymanski, 1974b)	2.293*	
Germanite (Tettenhorst and Corbató, 1984)		2.21
Germanite (three bonds/half-cell)		2.36
Germanite (three bonds/half-cell)		2.18
Germanite (three bonds/half-cell)		2.31
Germanite (three bonds/half-cell)		2.32

* The mean of the three equivalent bonds in low cubanite is 2.288 Å.

composition. The sphalerites in this study show no structural distortion suggesting other than random distribution of Cu or Fe atoms on the structural sites occupied by Zn atoms in pure ZnS. One can thus calculate from the partial molar volumes the corresponding fictive values of metal-S distances, which represent not any actual dimensions in the real structure, but rather the effective size of Fe or Cu atoms at the given composition. These values may be regarded as the contributions of the individual metals to the average site dimension in the structure.

Inspection of the contour diagrams in Figure 3 immediately reveals the important fact that the partial molar volumes (and corresponding fictive metal-S distances) of both the FeS and CuS components are controlled mainly by the content of the minor component, CuS. Furthermore, the value of the fictive Fe-S separation does not range widely and is significantly greater throughout the stability field of sphalerite solid solutions than observed tetrahedral Fe-S distances in any well-known Cu-Fe sulfide, as shown in Table 2. The fictive Cu-S distance, on the other hand, varies over a much larger range of values and is generally smaller than observed distances in geometrically similar sites in related structures (Table 2), except along the maximum Cu-rich stability limit of the sphalerite field. It appears, then, that as the Cu content of sphalerite increases, the apparent or effective size of the Cu atoms added increases to approximately the usual value at the limit of the field, whereas that of Fe decreases toward, but not to, its usual value. This approximately reciprocal relationship suggests the possibility of some sort of charge-transfer process, which may be analogous (in a doubtless oversimplified way) to the oxidation of Fe^{2+} by Cu^{2+}. It is possible that the accompanying changes in bonding may be related to the Cu-rich limit of the sphalerite phase field, for chalcopyrite and related minerals are probably characterized by a charge distribution more like Cu^{+}-Fe^{3+} than Cu^{2+}-Fe^{2+} (Shuey, 1975, p. 245), whereas the effective valence of Fe in sphalerite is presumably near 2+. It may be noted that the formal configuration $Cu^{+}Fe^{3+}$ is consistent with formation of hybrid sp^3 bonds with both atoms having 3d shells in favored states (half and full occupancy for Fe and Cu, respectively).

GEOLOGICAL CONSIDERATIONS

Geological considerations are paramount for the application of the sphalerite geobarometer, and unfortunately, the geological aspects of specific applications are not always discussed (or even known) in adequate detail. It is also sometimes overlooked that even if geologic constraints preclude rigorous application of the geobarometer in a particular instance, a careful study of sphalerite composition may well provide new insight into geologic processes of greater significance than the mere estimation of pressure.

One of the problems in the use of Figure 1 as a geobarometric guide for pyrite + pyrrhotite + sphalerite assemblages is the correct assignment of a temperature for last equilibration (consideration of the varying chemical parameters characterizing primary deposition from hydrothermal solutions only further complicates an already difficult array of problems). The sphalerite composition itself only assigns the sample to a specific temperature-pressure trajectory, which, as an inspection of Figure 2 will reveal, can represent a considerable range in pressures and temperatures.

Of course, if one assumes that the isobars really are vertical in Figure 1 (i.e., that sphalerite composition is independent of temperature), as advocated by Scott (1976) and accepted by most subsequent investigators, the assignment of temperature becomes immaterial. But as we have argued earlier, the isobars can in general be neither parallel nor vertical. Thus thermometry is important, and it is obviously necessary for the temperature estimated to be that at which the sphalerite equilibrated, which may not necessarily be the same as that estimated from silicate mineral assemblages, isotopic fractionation patterns, or other independent means of thermometry based on events whose relation to sphalerite equilibration cannot be demonstrated.

Let us consider just what is meant by the temperature of last equilibration. Suppose that the fractionation of O isotopes between intergrown quartz and magnetite records a reliable temperature of 600 °C for a plutonic event, perhaps a regional metamorphic event in which an assemblage of pyrite + pyrrhotite + sphalerite was formed simultaneously. We know (Barton and Toulmin, 1966) that sphalerite in particles 100 μm or less in diameter will equilibrate with pyrite and pyrrhotite in powdered form in about 1 yr at 600 °C; presumably a compact crystal mass (such as most ores) will react no more slowly. What will happen to this assemblage as it cools, perhaps spending 1 m.y. between 550 and 500 °C and 100 m.y. at 200 °C buried by 5 or 10 km of rock? This question was raised more than three decades ago by Lyon (1959), and it deserves restatement today. Indeed, the determination of diffusion coefficients (Mizuta, 1988a) now permits some quantitative modeling of such effects. Preliminary calculations indicate that retrograde effects will be significant in many geologic situations, in agreement with Mizuta's (1988a, p. 1218) calculated closing temperatures in the range of 150 to 350 °C depending on cooling rate and grain size.

As an example of the problems and opportunities that may arise, let us consider some features of a sediment-hosted massive sulfide deposit in a metamorphic terrane: Ducktown, Tennessee. Ringler (1979), among others, has applied the sphalerite geobarometer to core samples from the Calloway mine. Because it is our intention only to present an example, and not to discuss Ducktown per se, we will describe only a single specimen, from the 24 level of the Calloway mine. Many of the features critical to our discussion are widespread, though visible only in doubly polished thin section, from which the photos shown in Figure 4 were taken (see Heald-Wetlaufer et al., 1982, for a discussion of the technique).

Each field in Figure 4 is shown twice: in reflected and in transmitted light. The sphalerite varies continuously within individual crystals from yellow to red-brown (nearly white to gray in the photos), and electron microprobe analyses show that the color is a reliable index of relative Fe content, which ranges from 6.5 to 14 mol% FeS. The frequency distribution of sphalerite compositions is shown in Figure 5.

The sphalerite is associated with pyrrhotite, chalcopyrite, pyrite, galena, stannite, calcite, amphibole, biotite, and quartz. To identify the critical equilibrium mineral assemblages, we must first establish the temporal relations. Examination of the photos in Figure 4 clearly shows that the ore represents a process that never reached completion, superposed on an earlier, perhaps equilibrated, stage. The earlier stage may have developed during a metamorphic maximum that erased microscopic and textural evidence of the primary formation of these rocks. There is no evidence for growth-zoned sphalerite crystals of the sort described from unmetamorphosed massive-sulfide deposits (Eldridge et al., 1983), but rare grains of Cu-poor, chalcopyrite-free sphalerite may well have been chemically isolated grains whose initial, premetamorphic low-Cu composition has been preserved even through the major metamorphic event.

The most striking aspect of the sphalerite is the paragenesis and distribution of Fe-rich and less-Fe-rich varieties, summarized in Table 3. The yellow sphalerite (8–9% FeS) is found (1) along the contacts with larger masses of pyrrhotite, pyrite, and chalcopyrite, (2) along fractures and pyrrhotite- or chalcopyrite-bearing veinlets cutting sphalerite crystals, and (3) along some, but not all, grain boundaries against gangue. The red-brown sphalerite (12–14% FeS) occurs as cores of larger, unbroken crystals and as smaller, isolated crystals in the calcite gangue. Exsolved chalcopyrite may be present with any of the sphalerite, but it is much more abundant in the orange sphalerite intermediate in Fe content to the yellow and red-brown. Some red-brown sphalerite has no exsolved chalcopyrite at all, and the yellow sphalerite appears drained in the sense that coarse, intergranular chalcopyrite is found instead of the finer exsolved chalcopyrite. Obviously the yellow sphalerite is an alteration of the red-brown. Furthermore, the yellow sphalerite is clearly more nearly compatible with the environment of pyrite + pyrrhotite + chalcopyrite than is the more Fe-rich red-brown sphalerite.

It appears that the attempts of the system to readjust its state to a new equilibrium position for the assemblage sphalerite + pyrite + pyrrhotite + chalcopyrite were strongly confined to zones up to perhaps 100 μm wide that were associated with masses of chalcopyrite, pyrrhotite, or pyrite which served as solid-state pipelines and sinks for FeS diffusing out of the sphalerite. In addition, any fractures or grain boundaries that provided fluid films to connect sphalerite with Fe-bearing sulfides also served as a conduit for chemical migration. The cores of unbroken sphalerite grains, and entire sphalerite crystals that were chemically isolated and mechanically cushioned by

TABLE 3. Sphalerite types found within a single thin section from the 24 level, Calloway mine

Type	Description	Mol% FeS	Interpretation
1	Isolated grains in gangue; exsolved po and ccp very minor; color is even red-brown	12–14	Unaltered grains preserved since metamorphic maximum, or grains from which ccp has exsolved and been transported out of the plane of the section
2	Cores or unbroken parts of larger grains; grains may or may not be isolated in gangue; color is red-brown	12–14	Same as type 1
3	Interiors of grains with abundant fine ccp and/or po; color varies from red-brown to yellow	9–12	Recrystallized exsolved sulfides; sphalerite in transition from red-brown to yellow
4	Small (less than 100-μm grains of sp in a great excess of the other sulfides, py, po, or ccp; color is yellow	9	Reequilibrated with, or possibly exsolved from copper-iron sulfides
5	Sphalerite in contact with larger grains of py, po, or ccp, or as margins of some grains in contact with gangue, or along fractures within sp grains. Color is yellow; the po and ccp occur along grain boundaries with little as exsolution blebs	9	Same as type 4, but in addition to the neighboring py, po, or ccp, more distant py, po, or ccp participated in the reaction via grain-boundary plumbing
6	Rare paler yellow sp	6.5–9	Optimum retrograde conditions, distinction from type 4 uncertain

Note: Photographs of typical textures are shown in Figure 4. Abbreviations: sp = sphalerite; py = pyrite; po = pyrrhotite; ccp = chalcopyrite. All of these sphalerites contain 0.2 mol% CuS and CdS and 0.5 to 0.6 mol% MnS. The uncertainty for each is 0.2 mol%.

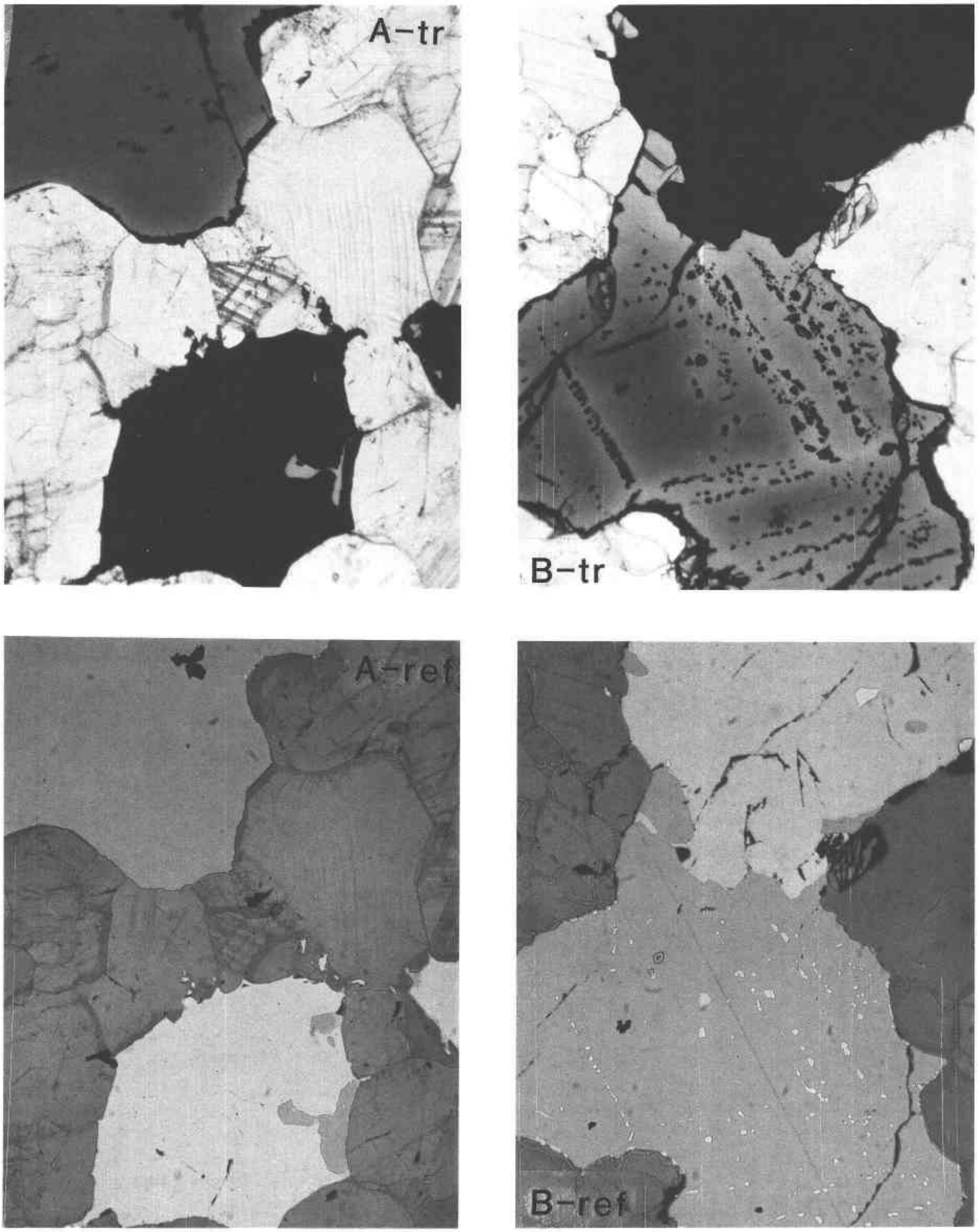
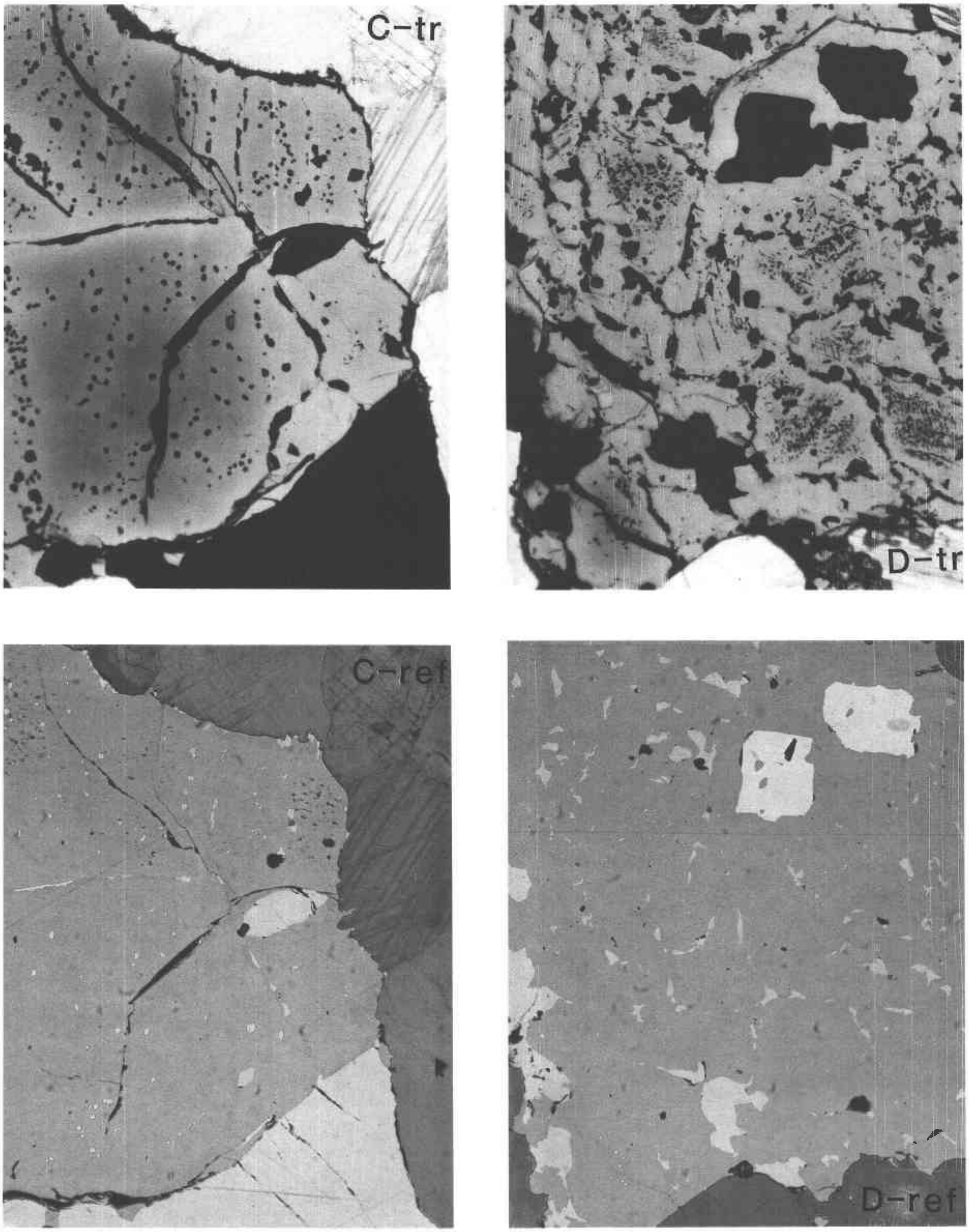


Fig. 4. Photographs of doubly polished sections of ore from the 24 level of the Calloway mine, Ducktown, Tennessee. Each field of view is approximately 1.0 mm in short dimension and is shown as a matched pair of photographs, one in transmitted (tr) and one in reflected (ref) light. Gangue, mostly calcite, is dark gray in reflected light and bright in transmitted. Sphalerite is dull gray in reflected light and variably transparent in transmitted light. Pyrrhotite is opaque in transmitted light and intermediate gray in reflected (**B**, **C**, and **D**). In **A** and **B**, the brightest phase in reflected light is chalcopyrite. (**A**) Part of a type I sphal-



erite grain isolated in calcite without retrograde compositional change. (**B**) Sphalerite grain whose margins adjacent to pyrrhotite and to gangue have decreased Fe content. (**C**) Similar to **B** but also shows depletion of Fe near fractures in sphalerite. (**D**) Two pyrite cubes (bright in reflected light) and smaller anhedra of pyrrhotite in a matrix of type V sphalerite. Note the resorption of the pyrite, presumably as the result of reaction with stoichiometric FeS from the sphalerite to yield additional pyrrhotite.

gangue (especially calcite), were preserved in their pristine chemical microenvironments.

Sphalerite grains of type 5 (Table 3) show smooth, continuous compositional gradients right up to many of the contacts with gangue (Fig. 4C) and to all contacts with the larger masses of pyrrhotite or chalcopyrite, which appear to be serving as reservoirs or sinks for FeS (Figs. 4B, 4C). The gradients are steepest, of the order of 0.05 mol% FeS/μm, at the contacts and pass asymptotically into type 2 sphalerite 50 to 100 μm from the contact. Such gradients are lacking adjacent to some small pyrrhotite or chalcopyrite grains, presumably because the smaller grains cannot consume significant amounts of FeS. If this model is correct, there should be correlations among the composition of the sphalerite, the mineralogy of the sulfide aggregates, the relative proportions of sphalerite, pyrrhotite, and chalcopyrite, the presence or absence of pyrite with the assemblage sphalerite + chalcopyrite + pyrrhotite, and the effective grain sizes involved. Of these variables, we have quantitative information only on the composition of the sphalerite; our observations on the others are purely qualitative and would require much more extended documentation than is practical for this commentary. S. D. Scott and coworkers have recognized this sort of complexity and have sought to deduce the initial metamorphic condition by examining sphalerite encapsulated in pyrite monocrystals. This approach, of course, precludes the reconstruction of postmetamorphic history from that assemblage.

An additional consequence of this model is that individual sulfide aggregates might behave as if they were isolated chemical systems, each leading to local equilibrium assemblages having a range of mineral compositions. Only in the divariant assemblage sphalerite + pyrrhotite + pyrite + chalcopyrite would the composition of the sulfides be uniquely fixed by the temperature and pressure. Part of the strong maximum on the histogram in Figure 5 correlates with sphalerite observed to be in close proximity to pyrrhotite + chalcopyrite + pyrite; the remainder represents grains that do not visibly contact the assemblage pyrrhotite + chalcopyrite + pyrite but must be in close communication via cracks and open grain boundaries.

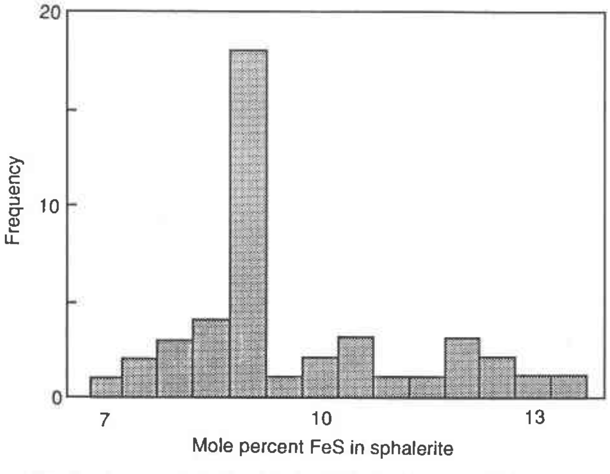


Fig. 5. Frequency distribution of sphalerite analyses from a single ore sample from the Calloway mine, Ducktown, Tennessee.

The sense of the compositional gradient at the margins of the sphalerite grains implies lowering FeS concentrations with time. This means that the temperature-pressure trajectory along which the reacting mineral assemblage traveled was one in which temperature decreased more rapidly than pressure relative to contours of sphalerite composition (a point also made, from a different direction, by Brown et al., 1978). One might argue that the gradients we see today could reflect reaction during increasing pressure at low temperature, but one would expect the eventual pressure release to be no slower than its increase, so a reaction rate fast enough to create the burial gradient should permit reaction to reverse it, at least partially. Improved knowledge of diffusion and reaction mechanisms in sphalerite (Mizuta, 1988a, 1988b) should permit more precise modeling to further our understanding of these textures.

To this point the discussion has considered only the Fe content of the sphalerite, but the Cu content is also of potential importance. Experimental work at low pressure (Wiggins and Craig, 1980; Hutchison and Scott, 1981; Kojima and Sugaki, 1984) shows that the Cu content of sphalerite from the assemblage sphalerite + pyrrhotite + pyrite + intermediate solid solution is a sensitive measure of temperature. Many, if not most, sphalerites analyzed in assemblages of sphalerite + pyrrhotite + pyrite + chalcopyrite (or intermediate solid solution) are so low in Cu that the Cu contents are just at the limit of microprobe sensitivity (about 0.2 mol% for the instrument at the U.S. Geological Survey). This means that such assemblages last reacted (equilibrated?) at some temperature below 400 °C, even if other thermometers such as silicate + oxide assemblages indicate much higher temperatures. When examined carefully the exsolved phase has usually proven to be chalcopyrite, (not the nonstoichiometric intermediate solid solution or its quench products, talnakhite, mooihoekite, haycockite, or cubanite) consistent with the fact that sphalerite conforms rather strictly to the stoichiometric ratio 1:1, metal:S. The commonly observed tie line between chalcopyrite and pyrrhotite is stable only below 334 ± 17 °C (Yund and Kullerud, 1966), reinforcing the notion of the low temperatures of reaction for most massive sulfide ores. Do chalcopyrite-forming reactions well below 400 °C mean that the whole of the sphalerite reequilibrated at low temperature, or perhaps only that chalcopyrite exsolved? We do not know, but it is obviously a question deserving further study.

One might logically ask whether high pressure during equilibration might be responsible for the low Cu concentration observed in sphalerite. The following argument indicates that this is unlikely. The pertinent reaction is

$$CuS_{sp} + FeS_{sp} = CuFeS_2. \quad (9)$$

The ΔV of this reaction can be evaluated from the partial molar volumes of CuS and FeS in sphalerite (Fig. 3) and the molar volume of chalcopyrite (Hall and Stewart, 1973). Under the usual range of sphalerite compositions (less than 35 mol% FeS) the ΔV term is negative, indicating that pressure does indeed try to squeeze chalcopyrite out of sphalerite. Presumably a similar relationship would prevail for the intermediate solid solution. However, the studies of Wiggins and Craig (1980) and Hutchison and Scott (1981) both show that the Cu content of sphalerite equilibrated with iss, pyrite, and pyrrhotite is so low (a few tenths of a percent) at temperatures high enough for geologically rapid reaction (450–500 °C) that the influence of temperature alone can be expected to produce the observed low content of Cu remaining in natural sphalerite. A low Cu content is not a guide to high pressure.

To summarize the Ducktown example, numerous lines of textural and compositional evidence show that reactions have proceeded to much lower temperatures than indicated by geothermometers based on the associated metamorphic rocks. The geometry of the regions representing the local equilibrium assemblage sphalerite + pyrrhotite + chalcopyrite + pyrite is very complex and involves the volumes occupied by the copper-iron sulfides and the sphalerite near their mutual contacts, plus sphalerite along certain grain boundaries and fractures that permitted communication with the copper-iron sulfides by means of a fluid medium. Isolated sphalerite crystals within 1 mm of those participating in the retrograde reactions involving sphalerite + pyrrhotite + pyrite + chalcopyrite may show no sign of reaction.

SUMMARY

At temperatures of 500 °C and above, the experimental and theoretical basis of the sphalerite geobarometer (pyrite + pyrrhotite + sphalerite assemblages) is reasonably well established in the system Fe-Zn-S. At these temperatures, the studies of Wiggins and Craig (1980) show significant (~1 mol%) increase in FeS content for sphalerite in equilibrium with the intermediate solid solution as well as pyrite and pyrrhotite, and so a given Fe content would correspond to a pressure even higher than that predicted by Scott (1973, 1976).

More serious problems arise with respect to the low-temperature part of the phase diagram, where more study is definitely needed. Below 500 °C, thermodynamic calculations and experimental results diverge for reasons that are not yet clear. It does seem clear, however, that low (e.g., 8–12 mol%) FeS content for sphalerite in the assemblage pyrite + pyrrhotite + chalcopyrite + sphalerite may be caused by either high pressure, as emphasized by Scott, or low temperature, with or without high pressure. Studies of the solubility of chalcopyrite in sphalerite and textural-compositional relations of sphalerite in a sample from Ducktown, Tennessee, suggest that the low-temperature environment has overprinted the high-temperature environment, possibly destroying the high-temperature record.

It is now widely recognized that uncritical, cookbook application of the sphalerite geobarometer generally leads to unsatisfactory results (see, e.g., commentary by Banno, 1988; Stumpfl, 1979, 1980; and Plimer, 1980). The importance of establishing the required equilibrium assemblage and the postformation history of the samples under study is more generally understood (see discussions by, among others, Jamieson and Craw, 1987; Boctor, 1980; and Bristol, 1979). Careful, detailed studies of well-chosen examples have, however, resulted in productive applications; we note, arbitrarily among others, the work of Browne and Lovering (1973), Brown et al. (1978), Shimizu and Shimazaki (1981), Moles (1983), and Stowell (1989). We emphasize, further, as Lattanzi (1980) has indicated, that the method has many positive attributes: the mineral association required is relatively simple and of widespread occurrence; complications of nonessential components are minor; it rests on a firm theoretical foundation and a considerable body of experimental data; and the kinetics of reactions involved are favorable for fruitful interpretation of geologic processes. The discrepancies between genetic conditions inferred from sphalerite compositions and from oxide-silicate equilibria may in many instances reflect the retention of elements of petrologic history otherwise unrecorded. The conflict between theory and experiment in the low-temperature, high-pressure region must be resolved, and the method must be applied with due care and attention to detailed textural relations among partially equilibrated regions, but the potential benefits amply warrant efforts to clear the reputation of an unjustly maligned tool.

HISTORY AND ACKNOWLEDGMENTS

This paper is based on a manuscript originally intended to be a companion paper to Hutchison and Scott (1981); through no fault of theirs, we are a bit tardy in presenting it. An informal summary of some of our results has been presented orally (Toulmin et al., 1984). We gratefully acknowledge stimulating discussions with Hutchison and Scott, and with J.R. Craig, D.B. Stewart, and Motoaki Sato, who reviewed various early versions of the manuscript. Many colleagues have contributed to our thoughts and corrected our mistakes over the years; we thank them all while absolving them of responsibility for the errors that remain. We are especially pleased to offer this paper to a volume dedicated to Jim Thompson, whose formulation of the theory of open systems in petrology provided the model for an approach to the study of ore-forming systems that has proved enormously fruitful over the last three decades.

REFERENCES CITED

Banno, Shohei (1988) On the sphalerite geobarometer. Geochemical Journal, 22, 129–131.

Barton, Paul B., Jr., and Toulmin, Priestley, III (1966) Phase relations involving sphalerite in the Fe-Zn-S system. Economic Geology, 61, 815–849.

Barton, P.B., Jr., Bethke, P.M., and Roedder, E. (1977) Environment of ore deposition in the Creede mining district, San Juan Mountains, Colorado: III. Progress toward interpretation of the chemistry of the ore-forming fluid for the OH vein. Economic Geology, 72, 1–24.

Birch, Francis (1966) Compressibility; elastic constants. Geological Society of America Memoir 97, 97–173.

Boctor, N.Z. (1980) Sphalerite geobarometry in Bodenmais ore, Bavaria. American Mineralogist, 65, 1031–1037.

Boorman, Roy S. (1967) Subsolidus studies in the ZnS-FeS-FeS_2 system. Economic Geology, 62, 614–631.

Bristol, C.C. (1979) Application of sphalerite geobarometry to ores from the Ruttan mine. Economic Geology, 74, 1496–1503.

Brown, P.E., Essene, E.J., and Kelly, W.C. (1978) Sphalerite geobarometry in the Balmat-Edwards district, New York. American Mineralogist, 63, 250–257.

Browne, P.R.L., and Lovering, J.F. (1973) Composition of sphalerites from the Broadlands geothermal field and their significance to sphalerite geothermometry and geobarometry. Economic Geology , 68, 381–387.

Bryndzia, L.T., and Scott, S.D. (1986) The sphalerite and hexagonal pyrrhotite geobarometer: Calibration and application. Geological Society of America Abstracts with Programs, 1986, 552.

Bryndzia, L.T., Scott, S.D., and Spry, P.G. (1988) Sphalerite and hexagonal pyrrhotite geobarometer: Experimental calibration and application to the metamorphosed sulfide ores of Broken Hill, Australia. Economic Geology, 83, 1193–1204.

——— (1990) Sphalerite and hexagonal pyrrhotite geobarometer: Correction in calibration and application. Economic Geology, 85, 408–411.

Chernyshev, L.V., and Anfilogov, V.N. (1967) Experimental data on the composition of sphalerite in association with pyrrhotite and pyrite from 350° to 500 °C. Doklady Akademiya Nauk SSSR, 176, 925–928 (in Russian).

——— (1968) Subsolidus phase relations in the ZnS-FeS-FeS_2 system. Economic Geology, 63, 841–844.

Chernyshev, L.V., Anfilogov, V.N., Pastushkova, T.M., and Suturina, T.A. (1968) Study of the Fe-Zn-S system in hydrothermal conditions. Geologiya Rudnykh Mestorozhdeniy, 10, 50–64 (in Russian).

Clifford, A.A. (1973) Multivariate error analysis, 112 p. Applied Science Publishers Ltd, London.

Craig, J.R., and Scott, S.D. (1974) Sulfide phase equilibria. Mineralogical Society of America, Short Course Notes, 1, CS-1–CS-110.

Eldridge, C.S., Barton, P.B., Jr., and Ohmoto, Hiroshi (1983) Mineral textures and their bearing on formation of Kuroko orebodies. Economic Geology Monograph 5, 241–281.

Ethier, V.G., Campbell, F.A., Both, R.A., and Krouse, H.R. (1976) The Sullivan ore body: I—Geological setting, and estimates of temperature and pressure of metamorphism. Economic Geology, 71, 1570–1588.

Evans, H.T., Jr., and Konnert, J.A. (1976) Crystal structure refinement of covellite. American Mineralogist, 61, 996–1000.

Fleet, M.E. (1968) On the lattice parameters and superstructures of pyrrhotites. American Mineralogist, 53, 1846–1855.

Gamble, Robert (1978) The sulfidation of andradite and hedenbergite: An experimental study of skarn-ore genesis, 243 p. Unpublished Ph.D. dissertation, Yale University, New Haven, Connecticut.

Groves, D.I., Binns, R.A., Barrett, F.M., and McQueen, F.G. (1975) Sphalerite compositions from Western Australian nickel deposits, a guide to equilibria below 300 °C. Economic Geology, 70, 391–396.

Hall, S.R., and Stewart, J.M. (1973) The crystal structure refinement of chalcopyrite, $CuFeS_2$. Acta Crystallographica, B29, 579–585.

Haraldsen, Haakon (1941) Ueber die Eisen(II)-Sulfidmischkristalle. Zeitschrift für anorgische und allgemeine Chemie, 246, 169–226.

Heald-Wetlaufer, P., Foley, N.K., and Hayba, D.O. (1982) Applications of doubly polished sections to the study of ore deposits. In Hagni, R.D., Ed., Process mineralogy II: Applications in metallurgy, ceramics, and geology, p. 451–468. American Institute of Mining and Metallurgical Engineers, New York.

Holdaway, M.J. (1971) Stability of andalusite and the aluminum silicate phase diagram. American Journal of Science, 271, 97–131.

Hutcheon, I. (1978) Calculation of metamorphic pressure using the sphalerite-pyrrhotite-pyrite equilibrium. American Mineralogist, 63, 87–95.

——— (1980) Calculated phase relations for pyrite-pyrrhotite-sphalerite: Correction. American Mineralogist, 65, 1063–1064.

Hutchison, M.N., and Scott, S.D. (1981) Sphalerite geobarometry in the Cu-Fe-Zn-S system. Economic Geology, 76, 143–153.

——— (1983) Experimental calibration of the sphalerite cosmobarometer. Geochimica et Cosmochimica Acta, 47, 101–108.

Jamieson, R.A., and Craw, D. (1987) Sphalerite geobarometry in metamorphic terranes: An appraisal with implications for metamorphic pressure in the Otago Schist. Journal of Metamorphic Geology, 5, 87–100.

Kalogeropoulos, S.I. (1983) Problems with the application of FeS in sphalerite coexisting with pyrite as an indicator of the fugacity of sulfur. Neues Jahrbuch, Mineralogische Mitteilungen, 2, 89–96.

Kissin, S.A., Schwartz, H.P., and Scott, S.D. (1986) Application of the sphalerite cosmobarometer to group IAB iron meteorites. Geochimica et Cosmochimica Acta, 50, 371–378.

Kojima, Shoji, and Sugaki, Asahiko (1984) Phase relations in the central portion of the Cu-Fe-Zn-S system between 800° and 500 °C. Mineralogical Journal, 12, 15–28.

Kullerud, Gunnar (1953) The FeS-ZnS system: A geological thermometer. Norsk geologisk tidsskrift, 32, 61–147.

Lachenbruch, A.H., and Sass, J.H. (1978) Models of an extending lithosphere and heat flow in the Basin and Range province. Geological Society of America Memoir 152, 209–250.

Lattanzi, P. (1980) A discussion of the paper by E.F. Stumpfl "Manganese haloes surrounding metamorphic stratabound base metal deposits." Mineralium Deposita, 15, 243–245.

Lusk, J., and Ford, C.E. (1978) Experimental extension of the sphalerite geobarometer to 10 kbar. American Mineralogist, 63, 516–519.

Lusk, J., Campbell, F.A., and Krouse, H.R. (1975) Application of sphalerite geobarometry and sulfur isotope geothermometry to ores of the Quemont Mine, Noranda, Quebec. Economic Geology, 70, 1070–1083.

Lyon, R.J.P. (1959) Time aspects of geothermometry. Mining Engineering, 11, 1145–1151.

Mizuta, Toshio (1988a) Interdiffusion rates of zinc and iron in natural sphalerite. Economic Geology, 83, 1205–1220.

——— (1988b) Compositional homogenization of sphalerite in hydrothermal ore deposits of Japan by post-depositional diffusion processes: With particular reference to metamorphosed Besshi-type deposits. Mining Geology, 38, 263–278.

Moles, N.R. (1983) Sphalerite composition in relation to deposition and metamorphism of the Foss stratiform Ba-Zn-Pb deposit, Aberfeldy, Scotland. Mineralogical Magazine, 47, 487–500.

Novikov, G.A., Sokolov, Yu.A., and Sipavina, L.V. (1982) The temperature dependence of the unit-cell parameters of pyrrhotite $Fe_{1-x}S$. Geokhimiya, no. 8, 1189–1194 (translated in Geochemistry International, 19, 4, 184–190).

Oberhänsli, R., Hofmann, B., and Gruner, U. (1985) Ein Massivsulfidvorkommen in der Trias der Präalpen. Schweizerische mineralogische und petrographische Mitteilungen, 65, 95–110.

Plimer, I.R. (1980) A discussion of paper by E.F. Stumpfl "Manganese haloes surrounding metamorphic stratabound base metal deposits." Mineralium Deposita, 15, 237–241.

Ringler, R.W. (1979) Sphalerite geobarometry of the Calloway mine, Ducktown, Tennessee. Economic Geology, 74, 937–942.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures (reprinted with corrections 1979). U.S. Geological Survey Bulletin 1452.

Schwarcz, H.P., Scott, S.D., and Kissin, S.A. (1975) Pressures of formation of iron meterorites from sphalerite compositions. Geochimica et Cosmochimica Acta, 39, 1457–1466.

Scott, S.D. (1973) Experimental calibration of the sphalerite geobarometer. Economic Geology, 68, 466–474.

——— (1976) Application of the sphalerite geobarometer to regionally metamorphosed terraines. American Mineralogist, 61, 661–670.

Scott, S.D., and Barnes, H.L. (1971) Sphalerite geothermometry and geobarometry. Economic Geology, 66, 653–669.

Scott, S.D., and Kissin, S.A. (1973) Sphalerite composition in the Zn-Fe-S system below 300 °C. Economic Geology, 68, 475–479.

Scott, S.D., Both, R.A., and Kissin, S.A. (1977) Sulfide petrology of Broken-Hill region, New-South Wales. Economic Geology, 72, 1410–1425.

Shimizu, M., and Shimazaki, H. (1981) Application of the sphalerite geobarometer to some skarn-type ore deposits. Mineralium Deposita, 16, 45–50.

Shuey, R.T. (1975) Semiconducting ore minerals, 415 p. Elsevier, New York.

Skinner, B.J. (1962) Thermal expansion of ten minerals. U.S. Geological Survey Professional Paper 450-D, D109–D112.

——— (1966) Thermal expansion. Geological Society of America Memoir 97, 75–96.

Skinner, B.J., White, D.E., Rose, H.J., Jr., and Mays, R.E. (1967) Sulfides associated with the Salton Sea geothermal brine. Economic Geology, 62, 316–330.

Stowell, H.H. (1989) Silicate and sulphide thermobarometry of low- to medium-grade metamorphic rocks from Holkham Bay, south-east Alaska. Journal of Metamorphic Geology, 7, 343–358.

Stumpfl, E.F. (1979) Manganese haloes surrounding metamorphic stratabound base metal deposits. Mineralium Deposita, 14, 207–217.

——— (1980) Reply to discussion by P. Lattanzi of Stumpfl (1979). Mineralium Deposita, 15, 247–249.

Szymanski, J.T. (1974a) A refinement of the crystal structure of cubanite, $CuFe_2S_3$. Zeitschrift für Kristallographie, 140, 218–239.

——— (1974b) The crystal structure of high-temperature $CuFe_2S_3$. Zeitschrift für Kristallographie, 140, 240–248.

Taylor, L.A. (1970) Fe-S system. Carnegie Institution of Washington Year Book, 68, 259–270.

Tettenhorst, R.M., and Corbató, C.E. (1984) Crystal structure of germanite, $Cu_{26}Ge_4Fe_4S_{32}$, determined by powder X-ray diffraction. American Mineralogist, 69, 943–947.

Thompson, J.B., Jr. (1967) Thermodynamic properties of simple solutions. In P.H. Abelson, Ed., Researches in geochemistry, vol. 2, p. 340–361. J. Wiley, New York.

Toulmin, P., III (1960) Effect of Cu on sphalerite phase equilibria—a preliminary report (abs.). Geological Society of America Bulletin, 71, 1993.

Toulmin, P., III, and Barton, P.B., Jr. (1964) A thermodynamic study of pyrite and pyrrhotite. Geochimica et Cosmochimica Acta, 28, 641–671.

Toulmin, P., III, Wiggins, L.B., and Barton, P.B., Jr. (1984) Volume relations in Cu-Fe-bearing sphalerite and implications for the "sphalerite geobarometer." Geological Society of America Abstracts with Programs, 16, 677.

Wiggins, L.B., and Craig, J.R. (1980) Reconnaissance of the Cu-Fe-Zn-S system: Sphalerite phase relationships. Economic Geology, 75, 742–751.

Yund, R.A., and Kullerud, G. (1966) Thermal stability of assemblages of the Cu-Fe-S system. Journal of Petrology, 7, 454–488.

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